Universal asymptotic behavior of critical dynamics in a nonionic micellar solution

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Dynamical critical behavior for a nonionic micellar solution of tetraethylene glycol *n*-decylether in water has been examined by the time-dependent correlation function measurements of scattered light close to its critical point of mixing. The asymptotic behavior in the decay rate is compared with the current prediction associated with a dynamic universal function proposed recently for a fluid system.

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I. INTRODUCTION

Much attention has been focused lately on the critical behavior in surfactant solutions with regard to critical-point universality as a fluid system [1]. Surfactant solutions including amphiphilic detergentlike monomers have dual tendencies because the surface-active molecule consists of a soluble hydrophilic region and an insoluble hydrophobic alkyl chain in water. A common family of surfactant molecules having the form $C_iH_{2i+1}-O-(CH_2-CH_2O)_iH$ is often referred to as C_iE_i. This dual nature causes them to undergo self-association leading to the formation of micelles in aqueous solution. Phase separation, demixing into micellar-poor and micellar-rich phases, can be induced at a certain region of the phase diagram by raising the temperature [2]. This suggests that interactions among micelles may play an important role in the phase separation of a micellar solution.

Corti and co-workers established that the increase in turbidity for a series of aqueous micellar solutions was the manifestation of critical opalescence, which should be attributed to the presence of concentration fluctuations near the critical mixing point [3]. From a light-scattering experiment, they found critical-like anomalies in the osmotic susceptibility χ_T and in the long-range correlation length ξ with power-law behavior but with the exponents dependent on the system. For example, they found the temperature dependences of $\chi_T \propto \epsilon^{-\gamma}$ and $\xi \propto \epsilon^{-\nu}$ with $\gamma \sim 1.25$ and $\nu \sim 0.63$ for C_6E_3 in water. However, they found the significantly different values of $\gamma \sim 0.88$ and $\nu \sim 0.44$ for $C_{12}E_8$ in water. Here $\epsilon = (T_c - T)/T_c$ is the scaled temperature normalized by the critical temperature T_c. Their results for the C_6E_3 in water were essentially the same as those obtained in earlier work by the authors for the same system [4]. Dietler and Cannell reexamined the critical behavior for the system $C_{12}E_8$ in water and observed three-dimensional Ising values for γ and ν near the critical mixing point, independent of whether the solvent was water or heavy water [5]. They also observed the same nonuniversal values of the exponents as did Corti and Degiorgio for $C_{12}E_8$ when they used a portion of the sample used by Corti and Degiorgio, and concluded that nonuniversal exponent values obtained by Corti and Degiorgio arose from the problems of sample itself. A detailed discussion is given in our recent paper [6]. Three-dimensional Ising-like values for the exponents γ and ν

also have been observed for $C_{12}E_6$ in water by Wilcoxon and Kaler [7]. In our work in [6] we obtained the universal exponents of $\gamma \sim 1.25$ and $\nu \sim 0.63$ for the present system of $C_{10}E_4$ in water [6]. Thus most of the nonionic micellar systems studied yield universal Ising-model exponents, but others exhibit possible discrepancies from the expected behavior for the fluid systems [8,9]. In this work we report that the diffusive decay of the fluctuations for a nonionic micellar solution of tetraethylene glycol *n*-decylether ($C_{10}E_4$) in water obeys asymptotically the dynamic universality of a fluid in the region very close to its critical point of mixing.

II. EXPERIMENT

Tetraethylene glycol *n*-decylether ($C_{10}E_4$) synthesized and purified by Nikko Chem. Co. Ltd. (lot no. 7003) and water of liquid chromatographic quality (Wako Pure Chem. Ind. Ltd.) were used without further purification. The critical weight fraction of the surfactant estimated from phase-equilibrium measurements [10] was $C_c = 0.02_2$, consistent with the value reported by Lang and Morgan [11], whereas the critical temperature $T_c = 292.4$ K was about 1.2 K lower than their value.

Dynamic light-scattering measurements were carried out for a critical composition of $C_{10}E_4$ in water by use of a 6-mm-diam cylindrical cell at four scattering angles of $\theta = 30°$, $60°$, $90°$, and $120°$ in the temperature range of $1.71 \times 10^{-5} \le \epsilon \le 3.16 \times 10^{-2}$. The scattered light was detected by a photon-counting method using an EMI 9863 photomultiplier tube and was analyzed by a 48-channel, single-clipped correlator (Malvern K7023). The optical alignment of the photometer and the test of the correlator were achieved using a centrifuged colloidal silica solution and a polystyrene latex solution [12]. The light-scattering photometer, the thermometer, sample preparations, and the details of experiments have been described fully elsewhere [7,10,13].

The observed autocorrelation function for $C_{10}E_4$ in water showed a systematic deviation from a single exponential decay in the region very close to the critical point of mixing, suggesting a significant multiple-scattering contribution [14]. Hence, we analyzed our autocorrelation function data with a quadratic polynomial [15]

$$\ln g(t) = K_0 - K_1 t + \tfrac{1}{2} K_2 t^2 . \tag{1}$$

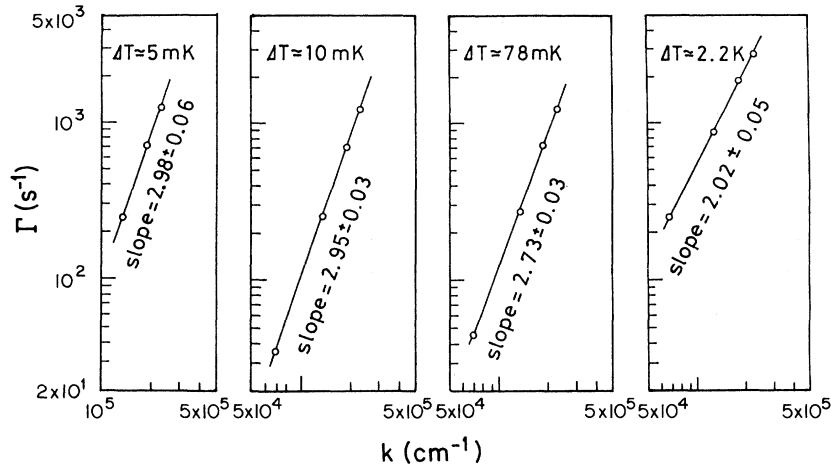FIG. 1. Decay rates as a function of the wave number k at fixed temperatures, in which the slope corresponds to the effective exponent $z_{eff}(T)$.

The first term, K_0, is an arbitrary factor in the normalization of $g(t)$. According to the double-scattering theories [14], the second term, K_1, may include a correction to the decay rate. The third one, K_2, may affect the curvature, including a possible correction factor due to higher-order contributions. If double-scattering contributions are mainly responsible for the observed deviations from a single exponential decay, then we may write $K_1 = (1 + \bar{\varepsilon}C_1)\Gamma$ and $K_2 = 2\bar{\varepsilon}C_2(\alpha)\Gamma^2$ with $\bar{\varepsilon}$ being the parameter proportional to the scattering light-path length of the medium. In our analysis, the parameters C_1 and $C_2(\alpha)$ are given by

$$C_1 = -0.14\gamma_0^{-1}(\ln\gamma_0 - 2.2), \qquad (2a)$$

$$C_2(\alpha) = 1.12\gamma_0^{-1}\frac{\ln\gamma_0 + 0.13}{1 + \alpha + \frac{9}{8}\alpha^2}, \qquad (2b)$$

where $\gamma_0 = 2r/h$, r and h are the radius of the sample cell and the height of the detector, respectively, $\alpha = (k_0\xi)^{-1}$, and k_0 is the incident wave number. We estimated $\bar{\varepsilon}C_1 \sim 10^{-3}$ and the parameter values are $\gamma_0 \sim 12$ and $\epsilon \sim 0.27$ for $T_c - T \sim 5$ mK. This allowed us to set $K_1 = \Gamma$. The numerical values used in the estimation associated with double-scattering corrections have been reported fully in Ref. [6].

III. RESULTS AND DISCUSSION

The dynamic theory [16] of critical phenomena predicts that the decay rate satisfies the asymptotic form $\Gamma \propto k^z$ in the region sufficiently close to the critical mixing point, where the wave number k is related to the scattering angle θ by the Bragg condition. The dynamical scaling exponent z is expected to satisfy the exponent relation $z = 3 + x_\eta$, where x_η is the dynamic viscosity exponent of the power law $\eta \propto \xi^{x_\eta}$ for the shear viscosity η. Values of x_η covering a range from 0.05 to 0.065 have been determined for many fluid mixtures. Our value of $x = 0.065 \pm 0.008$ for $C_{10}E_4$ in water is in excellent agreement with the currently accepted theoretical value of $x_\eta \sim 0.065$

[17]. The quoted error represents 1 standard deviation.

In order to estimate the value of z for $C_{10}E_4$ in water, we examine an effective exponent value $z_{eff}(T)$ at each temperature by $\Gamma \propto k^{z_{eff}(T)}$ as shown in Fig. 1. The effective exponent $z_{eff}(T)$ as a function of temperature should approach z in the limit of $T \to T_c$, while it should approach the value of 2 in the hydrodynamic region. This procedure is quite useful in the determination of the asymptotic value for z from decay-rate measurements. It was first applied successfully to establish the value $z = 3.063 \pm 0.012$, consistent with the current theoretical estimate, for 3-methylpentane in nitroethane by Burstyn and Sengers [18]. Their estimated error is 2 standard deviations [19]. Very close to the critical point $(T - T_c \sim 3$ mK) Chang et al. obtained the value $z_{eff} = 2.90 \pm 0.05$ for 3-methylpentane in nitroethane. Their value is in good agreement with our value $z_{eff} = 2.98 \pm 0.06$ at $T_c - T \sim 5$ mK for $C_{10}E_4$ in water. We show a plot of $z_{eff}(T)$ as a function of $T_c - T$ in Fig. 2. The values of z_{eff} obtained for $C_{10}E_4$ in water indeed approach the value 2 as predicted by the hydrodynamic law at high temperature, while
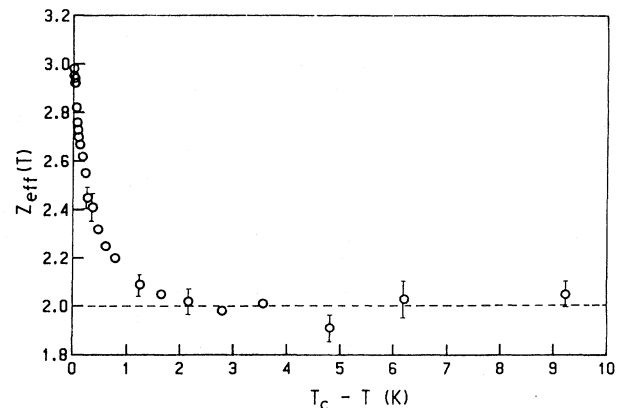

FIG. 2. Values of the effective exponent z_{eff} as a function of temperature difference $T_c - T$ from the critical point of mixing.
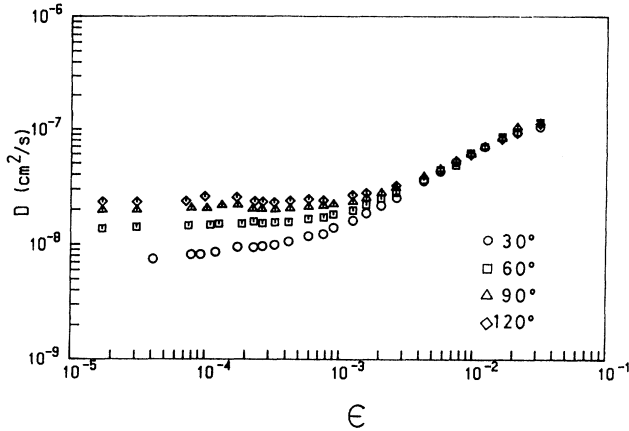
FIG. 3. Diffusion coefficients as a function of ϵ at $\theta = 30°$ (O), 60° (□), 90° (△), and 120° (◇).

FIG. 4. Scaled diffusion coefficient for the measured D as a function of the scaled variable $k\xi$. The solid curve represents the Kawasaki function and the dotted curve denotes the recently proposed dynamic scaling function with the theoretical estimation of $R = 1.03$ and $b = 0.55$.

z_{eff} suggests the relation $\Gamma \propto k^z$ with $z \sim 3$ in the asymptotic limit of $T \to T_c$. We estimated $z = 3.04 \pm 0.08$ in this asymptotic limit by fitting z_{eff} for $T_c - T < 0.2$ K to a smooth function of $T_c - T$. Our present result for the dynamic scaling exponent z for $C_{10}E_4$ in water is in good agreement with the universal value expected for a fluid system.

The diffusion coefficient $D(k) = \Gamma/k^2$ for $C_{10}E_4$ in water is shown in Fig. 3 as a function of ϵ. In the treatment of dynamic critical phenomena it is customary to separate the measured diffusion coefficient D into a nonsingular background contribution D_B and additional contribution D_C due to the critical fluctuations as $D = D_C + D_B$. This incremental diffusion coefficient can be represented by

$$D_C = [k_B T/6\pi\eta(T)\xi] \Omega(k\xi),\qquad(3)$$

where $R = \Omega(0)$ is a universal amplitude ratio associated with the dynamic scaling function $\Omega(y)$, which has a value slightly larger than unity and is given recently by [20]

$$\Omega(y) = \Omega_K(y)[S(y)]^{x_\eta},\qquad(4)$$

with the correction $S(y) = a_0(1 + b^2 y^2)^{1/2}$, and $\Omega_K(y)$ being the original Kawasaki function [21]. The correction $S(y)$ should approach a_0 in the limit $y \to 0$, which is related to the amplitude ratio R by $R = a_0^{x_\eta}$. The value of R has been determined recently, for example, as $R \sim 1.03$ by Burstyn et al. for 3-methylpentane in nitroethane [20], $R \sim 1.01$ by Guttinger and Cannell for Xe [22], and $R \sim 1.03$ by the authors for polydimethylsiloxane in diethylcarbonate [13]. In Fig. 4 we show a scaled diffusion coefficient D^* as a function of the scaled variable $k\xi$ for the measured D expressed by

$$D^* = [6\pi\eta(T)\xi/k_B T]D.\qquad(5)$$

Here the solid curve represents the original Kawasaki function and the dotted one the universal function expressed by Eq. (4) with the theoretical estimation of
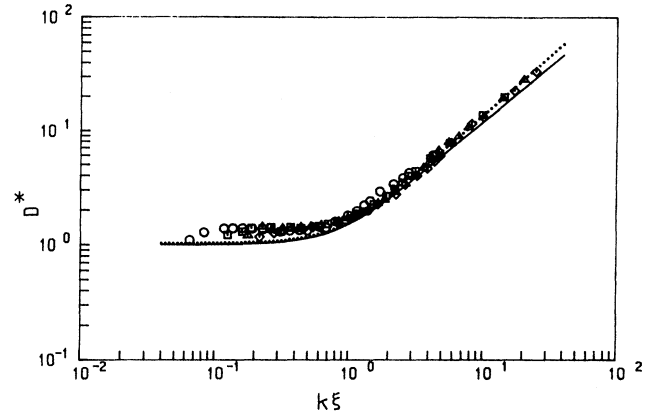
$R = 1.03$ and $b = 0.55$. Good agreement between the experimental results and the theoretical prediction is obtained in the critical region $k\xi > 1$. Systematic deviations from the theoretical curve at small $k\xi$, i.e., high-temperature region as seen in Fig. 4, should be attributed to a contribution due to the noncritical background term D_B. It may be expected that a relative contribution of D_B to D could be small in the region very close to the critical mixing point. In the present analysis, we have compared our experimental decay rate with two typical formulas for the dynamic scaling function in terms of the scaled quantity. As reported in earlier works [4,6,9], the background term in the measured diffusion coefficient could not be estimated easily for micellar solutions as it was for binary mixtures, which might depend on an effective molecular weight and/or a shape in aggregated micelles with a possible dependence on temperature and concentration. Details appear in a separate publication [23].

In this work we have examined two dynamical parameters z and R associated with the asymptotic behavior of the dynamic scaling function for a nonionic micellar solution of $C_{10}E_4$ in water in the region very close to its critical point of mixing. We have evaluated the dynamic scaling exponent to be $z = 3.04 \pm 0.08$. Our results suggest strongly that the diffusion coefficient for $C_{10}E_4$ in water obeys a recently proposed dynamic scaling function having the dynamic amplitude ratio R with a value slightly larger than unity very close to the critical mixing point.

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